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UMI
Environmental Effects on Some Mechanical Properties of Fibre Composites

By

Chang Qian

A thesis submitted in conformity with the requirements for the Degree of Master of Applied Science, Department of Chemical Engineering and Applied Chemistry, in the University of Toronto

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Abstract

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Department of Chemical Engineering and Applied Chemistry

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This study is carried out to investigate the effects of hot water, moderately strong acid and kerosene on the polymeric composite laminates. Diffusion was studied and the effects of these environmental agents on the transverse strength, the interlaminar strength, and the fracture toughness of these composite systems were examined.

It was found that the carbon-polyimide samples had lower water absorption and diffusion rates than the carbon-epoxy samples. Voids in the composites contained water, but did not fill with it. All the composites stood up well to the 60°C water treatment, but all except the NASA samples showed very significant transverse strength loss after prolonged immersion in 90°C water. The effect of 20% HCl appeared to be rather serious in the case of the carbon-epoxy, but the carbon-polyimide was less badly affected. In most cases, paraffin oil at 80°C had little effect. The CBS test method did not work very well for the wet samples.
# Table of Contents

Abstract i

Acknowledgements ii

Table of Contents iii

List of Tables vi

List of Figures vii

List of Nomenclature xiv

1. Introduction 1

1.1. Composite Materials 1

1.2. Polymers 2

1.2.1. Epoxies 5

1.2.2. Polyimides 6

1.3. Fibres 8

1.3.1. Glass 9

1.3.2. Carbon 10

1.4. Transverse Strength 10

1.5. Curved Beam Strength Test 12

1.6. Fracture Toughness 14

1.7. Environment Resistance 16

1.7.1. Effects on Mechanical Properties 16

1.7.2. Diffusion 18

1.8. Objective of This Study 22
2. Experimental Method

2.1. Materials

2.2. Composite Fabrication

2.3. Environmental Exposure

2.4. Composite Testing

2.4.1. Transverse Tensile Strength Testing

2.4.2. Curved Beam Strength Testing

2.4.3. Fracture Toughness Testing

2.5. Microscope Examination

3. Experimental Results

3.1. Moisture Absorption

3.1.1. Unidirectional Samples

3.1.2. Cross-ply Samples

3.1.3. Absorption in Strong Acid and Kerosene

3.2. Transverse Strength

3.3. Curved Beam Strength

3.4. Fracture Toughness

3.5. Image Analysis

3.5.1. SEM Observations

3.5.2. Fibre Volume Fractions

4. Discussion

4.1. Fluid Absorption

4.2. Transverse Strength
4.3. Curved Beam Strength

4.4. Fracture Toughness

5. Conclusions

6. References
# List of Tables

1.1 Comparison between conventional and composite material [2]  
2.1 Properties of the materials used  
3.1 Ratio of the inelastic/elastic deformation on the $\sigma_{20}$ tests  
3.2 Ratio of the maximum force : displacement (kN/mm) at the maximum force in the CBS tests  
3.3 Ratio of (the displacement at 20% of the maximum force / displacement at the maximum force) in the $K_{1L}$ tests  
3.4 Fibre volume fractions and densities of the unidirectional samples  
4.1 Diffusion data estimated from the water absorption plot  
4.2 Theory vs. experiment for voids filling with water
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Illustration of different polymer structures [4]</td>
<td>4</td>
</tr>
<tr>
<td>1.2</td>
<td>Epoxy reacts with a curing agent (DETA) and form a cross-linked network [12]</td>
<td>5</td>
</tr>
<tr>
<td>1.3</td>
<td>Structure of the most common used Epoxy, DGEBA [12]</td>
<td>6</td>
</tr>
<tr>
<td>1.4</td>
<td>Structure of a typical condensation polyimide [12]</td>
<td>7</td>
</tr>
<tr>
<td>1.5</td>
<td>Component reactants used in PMR-15 polyimide resin [12]</td>
<td>8</td>
</tr>
<tr>
<td>1.6</td>
<td>Internal structure of a carbon fibre, showing the arrangement of plans of carbon atoms [20]</td>
<td>10</td>
</tr>
<tr>
<td>1.7</td>
<td>Different transverse fracture models</td>
<td>12</td>
</tr>
<tr>
<td>1.8</td>
<td>Illustration of different fracture toughness models [1]</td>
<td>14</td>
</tr>
<tr>
<td>1.9</td>
<td>Illustration of the change of moisture content with the square root of time 20</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Section of mould which was used for curved beam strength test</td>
<td>24</td>
</tr>
<tr>
<td>2.2</td>
<td>Front and top views of curved beam strength sample</td>
<td>25</td>
</tr>
<tr>
<td>2.3</td>
<td>Illustration of water/kerosene bath system</td>
<td>27</td>
</tr>
<tr>
<td>2.4</td>
<td>Illustration of transverse tensile strength test sample</td>
<td>28</td>
</tr>
<tr>
<td>Page</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>Illustration of four-point-bending test apparatus</td>
<td></td>
</tr>
<tr>
<td>2.6</td>
<td>Illustration of translaminar fracture toughness test specimen and the test arrangement</td>
<td></td>
</tr>
<tr>
<td>2.7</td>
<td>Criterion for $K_I$; test on load verse displacement plot</td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>Moisture absorption of carbon-epoxy in 90°C and 60°C water</td>
<td></td>
</tr>
<tr>
<td>3.2</td>
<td>Moisture absorption of carbon-polyimide fabricated by Hexcel in the 90°C and 60°C water</td>
<td></td>
</tr>
<tr>
<td>3.3</td>
<td>Moisture absorption of the carbon-polyimide fabricated by NASA in 90°C and 60°C water</td>
<td></td>
</tr>
<tr>
<td>3.4</td>
<td>Moisture absorption of the lab-made carbon-polyimide in 90°C and 60°C water</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>Moisture absorption of the cross-ply carbon-epoxy in 90°C and 60°C water</td>
<td></td>
</tr>
<tr>
<td>3.6</td>
<td>Moisture absorption of the cross-ply lab-made carbon-polyimide in 90°C and 60°C water</td>
<td></td>
</tr>
<tr>
<td>3.7</td>
<td>Moisture absorption of the cross-ply glass-epoxy in the 20% HCl</td>
<td></td>
</tr>
<tr>
<td>3.8</td>
<td>Moisture absorption of the cross-ply carbon-epoxy in the 20% HCl</td>
<td></td>
</tr>
<tr>
<td>3.9</td>
<td>Moisture absorption of the lab-made cross ply carbon polyimide</td>
<td></td>
</tr>
</tbody>
</table>
in the 20% HCl

3.10 Absorption of the cross-ply carbon-epoxy in the 80°C kerosene

3.11 Absorption of the cross-ply carbon-polyimide in the 80°C kerosene

3.12 Typical force-displacement curves of the carbon-epoxy transverse strength tests: (a) in the 60°C water; (b) in the 90°C water

3.13 Effect of 60°C and 90°C water immersion on the transverse strength of the carbon-epoxy

3.14 Effect of 60°C and 90°C water immersion on the transverse modulus of the carbon-epoxy

3.15 Typical force-displacement curves of the Hexcel carbon-polyimide transverse strength tests: (a) in the 60°C water; (b) in the 90°C water

3.16 Effect of the 60°C and the 90°C water immersion on the transverse strength of the Hexcel carbon-polyimide

3.17 Effect of the 60°C and the 90°C water immersion on the transverse modulus of the Hexcel carbon-polyimide

3.18 Typical force-displacement curves of the NASA carbon-polyimide transverse strength tests: (a) in the 60°C water; (b) in the 90°C
<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.19</td>
<td>Effect of the 60°C and the 90°C water immersion on transverse strength of NASA carbon-polyimide</td>
<td>47</td>
</tr>
<tr>
<td>3.20</td>
<td>Effect of the 60°C and the 90°C water immersion on the transverse modulus of the NASA carbon-polyimide</td>
<td>47</td>
</tr>
<tr>
<td>3.21</td>
<td>Typical force-displacement curves of the lab-made carbon-polyimide transverse strength tests: (a) in the 60°C water; (b) in the 90°C water</td>
<td>48</td>
</tr>
<tr>
<td>3.22</td>
<td>Effect of the 60°C and the 90°C water immersion on the transverse strength of the lab-made carbon-polyimide</td>
<td>49</td>
</tr>
<tr>
<td>3.23</td>
<td>Effect of the 60°C and the 90°C water immersion on the transverse modulus of the lab-made carbon-polyimide</td>
<td>49</td>
</tr>
<tr>
<td>3.24</td>
<td>Typical force-displacement curves of the carbon-epoxy CBS tests: (a) in the 60°C water; (b) in the 90°C water</td>
<td>51</td>
</tr>
<tr>
<td>3.25</td>
<td>Effect of the 60°C and the 90°C water immersion on the CBS of the carbon-epoxy</td>
<td>51</td>
</tr>
<tr>
<td>3.26</td>
<td>Typical force-displacement curves of the carbon-epoxy CBS tests: (a) in the oil; (b) in the HCl</td>
<td>52</td>
</tr>
<tr>
<td>3.27</td>
<td>Effect of the oil and the HCl immersion on the CBS of the carbon-</td>
<td>52</td>
</tr>
</tbody>
</table>
3.28 Typical force-displacement curves of the lab-made carbon-polyimide CBS tests: (a) in the 60°C water; (b) in the 90°C water

3.29 Effect of the 60°C and the 90°C water immersion on the CBS of the carbon-polyimide

3.30 Typical force-displacement curves of the lab-made carbon-polyimide CBS tests: (a) in the oil; (b) in the HCl

3.31 Effect of the oil and the HCl immersion on the CBS of the lab-made carbon-polyimide

3.32 Typical force-displacement curves of the carbon-epoxy Fracture Toughness tests: (a) in the 60°C water; (b) in the 90°C water

3.33 Effect of the 90°C and the 60°C water immersion on the $K_{II}$ of the carbon-epoxy

3.34 Typical force-displacement curves of the carbon-epoxy Fracture Toughness tests: (a) in the HCl, and (b) in the oil

3.35 Effect of the oil and the HCl immersion on the $K_{II}$ of the carbon-epoxy

3.36 Typical force-displacement curves of the lab-made carbon-polyimide Fracture Toughness tests: (a) in the 60°C water; (b) in
3.37 Effect of the 90°C and the 60°C water immersion on the $K_{\text{II}}$ of the lab-made carbon-polyimide

3.38 Typical force-displacement curves of the lab-made carbon-polyimide Fracture Toughness tests: (a) in the HCl, and (b) in the oil

3.39 Effect of the oil and the HCl immersion on the $K_{\text{II}}$ of the lab-made carbon-polyimide

3.40 Typical force-displacement curve of the glass-epoxy Fracture Toughness tests in the HCl

3.41 Effect of HCl immersion on $K_{\text{II}}$ of glass-epoxy

3.42 Transverse fracture surface of the untreated carbon-epoxy sample

3.43 Transverse fracture surface of the carbon-epoxy sample after 2.5 kh in 90°C water

3.44 Transverse fracture surface of the untreated Hexcel carbon-polyimide sample

3.45 Transverse fracture surface of the Hexcel carbon-polyimide sample after 2.5 hr in the 90°C water

3.46 Transverse fracture surface of the untreated NASA carbon-polyimide sample
3.47  Transverse fracture surface of the NASA carbon-polyimide sample after 2.5 kh in the 90°C water

3.48  Cross-intersection images (X330) of: (a) the lab-made carbon-epoxy; (b) the lab-made carbon-polyimide; (c) the Hexcel carbon-polyimide and (d) the NASA carbon-polyimide

4.1  An absorption curve with constant diffusivity (NASA unidirectional Carbon-Polyimide sample in 90°C water)

4.2  A 2-stage absorption curve (unidirectional carbon-epoxy in 90°C water)
# List of Nomenclature

<table>
<thead>
<tr>
<th>CBS</th>
<th>Curved beam strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>Diameter of the CBS test loading bars or diffusion coefficient: subscript indicate stage, e.g. $D_1$</td>
</tr>
<tr>
<td>E</td>
<td>Young’s modulus: subscript indicate material, e.g. $E_t$</td>
</tr>
<tr>
<td>G</td>
<td>Work of fracture</td>
</tr>
<tr>
<td>K</td>
<td>Fracture toughness</td>
</tr>
<tr>
<td>M</td>
<td>Moisture content: subscript indicate stage, e.g. $M_1$</td>
</tr>
<tr>
<td>P</td>
<td>Packing factor or force or vapour pressure</td>
</tr>
<tr>
<td>R</td>
<td>Molar gas constant</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>V</td>
<td>Volume or volume fraction: subscripts indicate material, e.g. $V_t$</td>
</tr>
<tr>
<td>$a$</td>
<td>Size of crack</td>
</tr>
<tr>
<td>$b$</td>
<td>Half of the length of each side of the smallest repeating square unit in a composite</td>
</tr>
<tr>
<td>$c$</td>
<td>Concentration of diffusant, with subscripts indicating the stages, e.g. $c_t$, $c_m$</td>
</tr>
<tr>
<td>d</td>
<td>Distance; subscripts indicate direction, e.g. $d_1$</td>
</tr>
<tr>
<td>h</td>
<td>Thickness of the absorption specimen</td>
</tr>
<tr>
<td>l</td>
<td>Length of the absorption specimen</td>
</tr>
<tr>
<td>n</td>
<td>Width of the absorption specimen</td>
</tr>
<tr>
<td>r</td>
<td>Radii: subscripts indicate the positions, e.g. $r_t$</td>
</tr>
<tr>
<td>t</td>
<td>Time or specimen thickness</td>
</tr>
<tr>
<td>x</td>
<td>Space coordinate in direction of sheet thickness</td>
</tr>
</tbody>
</table>
\( \nu \) Poisson’s ratio

\( \rho \) Density

\( \sigma \) Tensile strength: subscript indicate direction or material, e.g. \( \sigma_x \)

Subscripts

1,2,3 Direction or stage

c Composite

t Fibre

i Interface or initial, or inner

m Matrix

o outer

p Polymer

r Radial direction

s Saturation

U Ultimate

w Water

Y Yield

x,y,z Directions

\( \theta \) Tangential direction
1 Introduction

1.1 Composite Materials

Structural materials can normally be divided into four categories: metals, polymers, ceramics, and composites [1]. Composites, which consist of two or more separate materials combined in a macroscopic structural unit, are made from various combinations of the other three materials. The concept of composite materials is not new. Nature is full of the examples of composites. The coconut palm leaf, for example, is a cantilever using the concept of fibre reinforcement. Wood is a fibrous composite with cellulose fibres in a lignin matrix. The cellulose fibres have high tensile strength and Young’s modulus but are very flexible because of their small diameters. The lignin matrix holds the fibres together so that the resulting material has a moderately high stiffness.

Just like the coconut palm leaf, the advanced composites are the blends of two or more materials. This kind of composite material is composed of the stiff, long fibres and a matrix that holds the fibres in place. The strength and stiffness of the fibres are much greater than those of matrix materials. When the fibre and the matrix are joined together, they both retain their individual identities but both influence the composite’s final properties directly. The resulting composite usually consists of layers, or lamina, of the fibres and the matrix stacked in a way to obtain the desired properties in one or more directions. In such a way, the high strength-to-weight or modulus-to-weight ratios of the composites can be achieved. The composite materials have other advantages, as well as some disadvantages. The advantages include [2]:

- Lower weight
Tailorable properties (strength or stiffness can be tailored to be in the load direction)

- Longer life (resist corrosion)
- Lower manufacturing costs because of reduction of parts number

The disadvantages include:

- Weakness of transverse properties
- Low toughness
- Hydrothermal degradation of matrix [3]

Thus, how to solve those problems became the major concern of composites research. Studies were conducted to understand the composites transverse properties, fracture toughness and hydrothermal effects on composites.

Table 1 gives a comparison of tensile properties of some metallic materials and structural composites. The advantages of composite materials are clearly indicated by the superior values of $E/\rho$ and $\sigma_t/\rho$.

### 1.2 Polymers

A polymer is a material which is composed of the comparatively simple recurring units. The polymers exist in three major forms: linear, branched, and cross-linked. A linear polymer is simply a chain of "mers". A branched polymer consists of a primary chain of the mers with other chains attached in three dimensions like a tree (see Figure 1). A cross-linked polymer has a large number of the three-dimensional interconnected chains.
<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>( \rho ) (kg/l)</th>
<th>E (GPa)</th>
<th>( \sigma_U ) (MPa)</th>
<th>( \sigma_Y ) (MPa)</th>
<th>( \frac{E}{\rho g} ) ((10^6 \text{ M}))</th>
<th>( \frac{\sigma_U}{\rho g} ) ((10^3 \text{ M}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAE 1010 steel (cold-worked)</td>
<td>7.87</td>
<td>207</td>
<td>365</td>
<td>303</td>
<td>2.68</td>
<td>4.72</td>
</tr>
<tr>
<td>AISI 4340 steel (quenched and tempered)</td>
<td>7.87</td>
<td>207</td>
<td>1722</td>
<td>1515</td>
<td>2.68</td>
<td>22.3</td>
</tr>
<tr>
<td>Al 6061-T6 aluminium alloy</td>
<td>2.70</td>
<td>68.9</td>
<td>310</td>
<td>275</td>
<td>2.60</td>
<td>11.7</td>
</tr>
<tr>
<td>Al 7178-T6 aluminium alloy</td>
<td>2.70</td>
<td>68.9</td>
<td>606</td>
<td>537</td>
<td>2.60</td>
<td>22.9</td>
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<tr>
<td>Ti-6Al-4V titanium alloy (aged)</td>
<td>4.43</td>
<td>110</td>
<td>1171</td>
<td>1068</td>
<td>2.53</td>
<td>26.9</td>
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<tr>
<td>L7-7 PH stainless steel (aged)</td>
<td>7.87</td>
<td>196</td>
<td>1619</td>
<td>1515</td>
<td>2.54</td>
<td>21.0</td>
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<tr>
<td>INCO 718 nickel alloy (aged)</td>
<td>8.2</td>
<td>207</td>
<td>1399</td>
<td>1247</td>
<td>2.57</td>
<td>17.4</td>
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<tr>
<td>High-strength carbon fibre-epoxy (unidirec-</td>
<td>1.55</td>
<td>137.8</td>
<td>1550</td>
<td></td>
<td>9.06</td>
<td>101.9</td>
</tr>
<tr>
<td>tional)*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>High-modulus carbon-epoxy (unidirec-</td>
<td>1.63</td>
<td>215</td>
<td>1240</td>
<td></td>
<td>13.44</td>
<td>77.5</td>
</tr>
<tr>
<td>tional)*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E-glass fibre-epoxy (unidirectional)*</td>
<td>1.85</td>
<td>39.3</td>
<td>965</td>
<td></td>
<td>2.16</td>
<td>53.2</td>
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<tr>
<td>Kevlar 49 fibre-epoxy (unidirectional)*</td>
<td>1.38</td>
<td>75.8</td>
<td>1378</td>
<td></td>
<td>5.60</td>
<td>101.8</td>
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<tr>
<td>Boron fibre-6061 Al alloy (annealed)</td>
<td>2.35</td>
<td>220</td>
<td>1109</td>
<td></td>
<td>9.54</td>
<td>48.1</td>
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<tr>
<td>Carbon fibre-epoxy (quasi-isotropic)</td>
<td>1.55</td>
<td>45.5</td>
<td>579</td>
<td></td>
<td>2.99</td>
<td>38</td>
</tr>
</tbody>
</table>

* In fibre direction

Note:

\( \rho \) = Density

E = Modulus

\( \sigma_U \) = Tensile strength

\( \sigma_Y \) = Yield strength

g = gravitational constant
Figure 1.1 Illustration of the different polymer structures [4]

The polymers are structurally much more complex than the metals or the ceramics. They are easily processible. On the other hand, the polymers have a lower strength and modulus and lower temperature use limits. Prolonged exposure to ultraviolet light [5] and some solvents [6] can cause the degradation of the polymer properties [7].

Polymers can be categorized into two types: thermoplastics and thermosets. Thermoplastics are the polymers have branches but not cross-link very much. Thus, they can be repeatedly softened by heating and hardened by cooling. Nylon, polyethylene and polysulfone are common examples of thermoplastics. Thermosets are polymers that are chemically reacted irreversibly cross-linked into a three-dimensional network. Examples of thermosets include epoxies and phenolics.

Due to differential thermal shrinkages, high performance composites normally contain residual stresses. However, the additives can put this shrinkage under control [8, 9].
1.2.1 Epoxies

The term "epoxy resin" refers to both the prepolymers and the cured resins. The prepolymers contain the reactive epoxy groups which gives their name:

This epoxy group is a three-member ring with two carbons and an oxygen and provides cross-link ability and good adhesion with a solid surface. Although the epoxy resins were firstly synthesized as early as 1891, it was not until the 1940s that the commercial epoxy resins were marketed. The earliest epoxy resins marketed were the reaction products of bisphenol A and epichlorohydrin and this is still the major route for the most epoxy resins today [10]. Figure 2 shows how the epoxy reacts with a typical amine curing agent (di-ethylene triamine, DETA) and form a cross-linked network. Many epoxy systems have been developed to fit the different requirements. The epoxy resin most commonly used is show in Figure 3.

Figure 1.2  Epoxy reacts with a curing agent (DETA) and form a cross-linked network [11]
Figure 1.3 Structure of the most common used Epoxy, DGEBA [11]

Compared to other important industrial polymers, the market size of the epoxy resins is relatively small, hence their price is higher. Many of the applications involve the high added value products, such as the advanced composites.

1.2.2 Polyimides

For the high temperature composite applications, the epoxy resins are inadequate and the polyimide resins are more suitable [12]. Polyimides are the polymers containing the cyclic imide groups in the main macromolecular chain.

Depending on the structure of the radicals attached to the imide group, polyimides can be of linear or three-dimensional structure. Some polyimide resins can be used up to a temperature of 316 °C [11]. Because of their high price, the polyimides have predominantly been used in the high quality and performance applications such as aerospace. Three important classes of polyimide resins have been used as the composite matrices:

- Condensation polyimides
- Polymerization of monomeric reactants (PMR) polyimides
• Bismaleimides (BMI)

Figure 4 shows the structure of a typical condensation polyimide. $R'$ and $R$ can be selected to obtain the different properties. The condensation polyimides exhibit outstanding thermal stable properties when exposed to the thermooxidative environments.

![Figure 4: Structure of a typical condensation polyimide](image)

PMR polyimides was originally developed by NASA. The PMR resin contains the monomeric reactants which are soluble in the easily removable solvents. To make the PMR prepgs, the solvent is first removed at relatively low temperature, then the temperature is raised to partly cure the resins: at the final step, the high temperature is used to complete the cross-linking procedure. One of the most serious disadvantages of this class of materials is the brittleness and the low fracture toughness.
Figure 1.5 Component reactants used in the PMR-15 polyimide resin [11]

The baseline bismaleimide (BMI) is formed by the reaction of a diamine with the maleic anhydride:

![Diagram of BMI reaction]

The BMIs normally are not as thermally stable as the condensation or the PMR polyimides, but are much better than the epoxies. The BMIs combine the advantages of thermal stability of polyimides and the easy processing of the epoxy and therefore are the good candidates for the aerospace use [11].

1.3 Fibres

The reinforcement materials include carbon, boron, glass, silicon carbide, alumina, and aramid fibres. The fibres are the key element which bears the major load in the composite materials. Theoretically, the glass has a very high strength, but for the daily
used glass (such as windows) the strength is normally only about 70 MPa. The reason behind this phenomenon is that there are millions of tiny cracks on the surface of the ordinary glass. However, in the form of the glass fibres, we can get an almost flaw-free glass surface, thus, the glass fibres with a strength of 3 GPa or more can be obtained [13]. This is the reason why the fibre composite materials can be so strong. However, without the fibre-polymer interface, the force cannot be transferred properly to the fibres [14]. The carbon and the glass fibres are widely used. These two materials will be discussed in turn.

1.3.1 Glass

The glass refers to wide range material which usually contains more than 50% of silica with random structures. Ordinary glass is the SiO₂ contains 14% Na₂O, 10% CaO, 2.5% MgO, 0.6% Al₂O₃, and 0.7% SO₂. For the reinforcement purposes, the F₂-glass is the most commonly used one with 17.5% CaO, 14.4% Al₂O₃, 8% B₂O₃, 4.5% MgO, 0.5% K₂O, 0.4% Fe₂O₃, 0.3% F₂ and 54.4% SiO₂ [15]. The sizing materials are normally coated on the surface of the glass fibres immediately after forming as a protection from the mechanical damage. Different measurement methods had been developed to help improving the glass interface [16]. The glass fibres used in the composites are usually coated [17] to ensure a good adhesion between the fibre and the matrix when the fibres are later incorporated in a polymer [18]. The sizing usually contains a coupling agent which is usually an organosilane with the structure X₃SiR. One of the advantages of the glass fibre is that its price is much lower than the other high-performance fibres [11].
1.3.2 Carbon

The carbon fibres are manufactured by treating the organic fibres (precursors) with the heat and tension, leading to a highly ordered carbon structure. The structure of a typical carbon fibre is illuminated at Figure 6. The surface of the fibre is usually oxidized to increase the adhesion of the matrix to the fibre. These treatments can be wet chemical treatment with the sodium hypochlorite or the nitric acid. They produce two effects on the carbon fibre: first, an outer, weak fibre surface is removed; second, the surface oxygen groups are added which can interact with the resin matrix [11].

![Figure 1.6](image)

Figure 1.6 Internal structure of a carbon fibre, showing the arrangement of planes of the carbon atoms [19]

1.4 Transverse Strength

Transverse strength is an important property because, being matrix dominated, they are generally weak. Thus, for example, a cross-ply laminate can start to fail at a relatively low stress by the transverse cracking. This is because the 90° layers generally have
a lower failure strain than the $0^\circ$ layers. Also, the interlaminar weakness causes the edge
delamination at the relatively low strains, and impact can induce the delamination as
well.

The composites with a weak fibre-matrix interface perform badly with respect to the above properties. Lots of efforts have been put into to improve the strength of the inter-
face [20].

If $\sigma_i$ is the interfacial tensile strength and $\sigma_i < \sigma_{mu}$ the failure occurs as shown in
Figure 1.7a and the transverse strength can be expressed by [20]:

$$\sigma_{tu} = \tau \sqrt{\frac{V_t}{P_t}} \sigma_i + \left[1 - 2 \sqrt{\frac{V_t}{P_t}}\right] \sigma_{mu} \tag{1}$$

Where $P_t$ is the packing factor and $P_t = \pi$ for the square packing and $2\pi \sqrt{3}$ for the
hexagonal packing. $V_t$ is the fibre volume fraction. $\sigma_{2u}$ is the ultimate transverse tensile
strength and $\sigma_{mu}$ is the ultimate matrix tensile strength.

When the interface is very strong, the crack will develop through the matrix (see
Figure 7b), then

$$\sigma_{tu} = \sigma_{mu} \tag{2}$$

Finally, the fibres can fail transversely, as shown in Figure 7c, this gives:

$$\sigma_{tu} = l' \sigma_{tu} + l' \sigma_{mu} \tag{3}$$

Where $\sigma_{tu}$ is the transverse tensile strength of the fibre.

Chan and Piggott studied the transverse strength of the unidirectional carbon-epoxy [20]. Their results showed that for the lab-made AS+epoxy composite, the $\sigma_{2u}$
value was 29±7 MPa when $V_1 = 0.4$. Meanwhile, the test result showed that the $\sigma_{mu}$ value was 49±3 MPa. The bare fibre surfaces on the SEM pictures suggested it was a bond failure due to the relatively weak interface. They also investigated the commercial carbon-epoxy laminates from Bombardier Aerospace, which gave a $\sigma_{2u}$ values of 51±3 MPa. The SEM pictures suggested a matrix failure because no bare fibres could be seen. This conclusion was confirmed the high value of $\sigma_{2u}$ (51±3 MPa), which is close to the expected polymer strength.

![bond failure](a) ![matrix failure](b) ![fibre failure](c)

**Figure 1.7 Different transverse fracture models**

### 1.5 Curved Beam Strength Test

The delamination is another important failure mode in the composite laminates [21, 22]. At and near the free edges (extending a distance approximately equal to the laminate thickness) of a laminate under stress, there is a three-dimensional state of the stress. Under the certain circumstances, there can be present rather large interlaminar stress at the free edge and thereby cause the failure. Normally, a delamination grows in a stable manner until it reaches a critical size, then further growth can occur in an unstable manner. The stresses near the edge include out of plane shear, $\tau_{xz}$, and compression, $\sigma_z$. 
There are many tests used to measure the apparent interlaminar shear strength to understand the resistance to delamination (e.g. ASTM D5389, D5448, D2344 and D4255).

However, it has been suggested that the composites do not fail in shear. Instead the failure is tensile. To measure this tensile stress, the curved beam testing method was developed. Wisnom et al. [23] used a curved beam testing four point bending to measure the interlaminar tensile strength and a short straight beam loaded in three point bending to measure the apparent interlaminar shear strength. Their study showed significant size effect on the interlaminar properties. The average interlaminar tensile strength dropped from 109 MPa for the thinnest specimens (16 plies with a thickness of 2 mm) to 61 MPa for the thickest (64 plies with a thickness of 8.5 mm). It was found that the apparent interlaminar shear strength was reduced from 97 MPa to 85 MPa. This is an illustration of the well-known phenomenon that the larger specimen contains more defects than the small ones.

ASTM published a new test standard, ASTM D6415, to quantify the interlaminar tensile strength [24]. For this, an “L” shape specimen, which is 25±1 mm wide with an inner radius of 6.4±0.2 mm at the bending area, is used. This method measures the Curved Beam Strength (CBS) which represents the moment per unit width that causes a delamination.

The specimen is flexed in four-point bending. An out of plane (through the thickness) tensile stress is produced in the curved region of the specimen using the test method. Circumferential tensile stress is produced along the inner surface, and compressive stresses are produced on the outer surface. The radial tensile stress ranges from zero at the inner and outer surfaces to a peak in the middle of the thickness where the delamination happens. By measuring the maximum bending force and displacement, the
nation happens. By measuring the maximum bending force and displacement, the CBS were calculated using:

\[
CBS = \left[ \frac{P}{2w \cos(\phi)} \right] \left[ \frac{d_i}{\cos(\phi)} + (D + t)\tan(\phi) \right]
\]  

(4)

Where:

\[
\phi = \sin^{-1} \left[ -d_i (D + t) + d_i \sqrt{d_i^2 + d_i^2 - D^2 - 2Dt} \right] \left[ d_i^2 + d_i^2 \right]
\]  

(5)

\[
d_i = d_i \tan(\phi_i) + \frac{D + t}{\cos(\phi_i)} - \Delta
\]  

(6)

Where \( P \) is the force, \( w \) is the width of sample, \( d_i \) is the horizontal distance between the centrelines of the two top and bottom adjacent rollers, \( D \) is the diameter of the cylindrical loading bars, \( t \) is the specimen thickness and \( \Delta \) is the displacement.

1.6 Fracture Toughness

![Illustration of different fracture toughness models](image)

**Figure 1.8** Illustration of different fracture toughness models [1]
Toughness is a measure of the difficulty to propagate a crack [25, 26]. There are three basic modes of crack extension (see Figure 8) and Mode I is the major concern in research.

Facture toughness, $K$, is a material property that can be determined experimentally:

$$K = \frac{\sigma \sqrt{\pi a}}{}$$

(7)

Where $\sigma$ is applied stress at failure and $a$ is the crack length.

If the fracture toughness of the material is known, Equation 7 can be used to determine the applied stress or the crack size if the other one is known.

$G$, the work of fracture, is another material property. $G$ is a useful tool in fracture study and it is relatively easy to measure under certain circumstances. In case of the isotropic material, $G$ and $K$ can be related with the equation:

$$G = (1 - v^2)K^2 / E$$

(8)

where $v$ is the Poisson’s ratio.

In the case of a dynamic situation, the toughness can be evaluated by the amount of energy absorbed during the impact until specimen failure. The dynamic toughness of the composite materials can be assessed by Falling Dart and Izod impact testing. In a quasi-static situation, in which the load is applied relatively slowly, the toughness may be evaluated by the area under the stress-strain curve up to the fracture point produced by a standard tensile test [27].

To test the fracture toughness of composite materials, a new ASTM standard E1922-97 was used. $K$ was measured with a narrow notch cut with a jeweller’s saw. The crack opening displacement was monitored while the specimen was pulled. $K$ was calcu-
lated from the maximum force. For a \([90, -45, 0, +45]_4t\) AS4 carbon-epoxy laminate, the
K was found to be 57±3 MPa m\(^{1/2}\). The corresponding G was 73±8 kJm\(^{-2}\).

1.7 Environment Resistance

1.7.1 Effects on Mechanical Properties

The increasing use of the fibre reinforced organic matrix composites in a structural applications requires that the responses of such materials to the environmental exposure be understood [28, 29, 30, 31, 32]. This in turn requires the analytical and experimental methods that predict the changes in the properties of the materials during the exposure to an ambient in which the environmental factors vary [33]. The effect of moisture has been the major concern of most researchers since the composite materials were used extensively in various industrial sectors over the past decades [34] and it was found the environmental exposure could change the glass transition temperature of composites [35]. The transverse properties of the composites can be affected by the environmental treatment relatively easily because they are mainly matrix determined [6]. The interlaminar properties and the fibre-matrix interface were also found to be affected by the environmental exposure [36, 37].

Studies showed that the environmental exposure had a strong influence on the transverse tensile strength. The environmental effects on the interface of the carbon-epoxy have been investigated [20]. The tensile strength of a commercial sample reduced by 50\% (from 50 MPa to 25 MPa) after 1.5 kh of immersion in 90°C water.

One of the most important consequences of the moisture absorption is a reduction in the glass transition temperature (\(T_g\)), of the resin as a result of water plasticization.
Jones studies $T_g$ in the epoxy resin and found that the average decrease, $\Delta T_g$, is approximately 20K for each 1% of moisture absorption. And for most epoxy resin for the aerospace application, in which the high degree of crosslink limit the water absorption, $\Delta T_g \geq 50K$. However, for the bismaleimide PMR-15, $\Delta T_g = -1.3 K \%^{-1}$ with an equilibrium moisture content of 1.3% at 96% RH [38]. Staunton also tested the effects of moisture on the glass transition temperature of the epoxy resins. His data showed that the $T_g$ reduced as much as 100K after epoxy absorbed 8% water [39].

The thermal strains are generated in the composite materials due to the mismatch in the thermal expansion coefficients of the fibre and resin. The absorption of moisture into the resin swells the resin matrix and tends to negate the thermal strains. For a polyester resin based composite studied by Jones, a reduction in the thermal strain by 0.2% occurs with a 0.6% increase in the water content. These results were obtained by recording the change in a curvature of the 0°/90° beam with time of immersion in water. He also found that in this case, a thermal residual strain is still present in the wet laminate but in other systems, where the water absorption is higher, the residual strain can be totally negated [37].

Normally, the moisture attacks the matrix and the fibre-matrix interface, however, there may be a destruction of the fibre surface due to the breaking of the polar bonds by chemical reaction, which also promotes pitting in the glass fibres. The organic fibres, such as Kevlar and wood fibres, also absorb moisture, tend to exhibit softening and may even crack internally. Another example is the environmental stress corrosion cracking, which is the delayed brittle fracture of a stressed material under the influence of an environmental agency. For the composite materials, it has mainly been reported for the E-
glass composites in an acidic environment. This is because the leaching of the network modifiers occurs simultaneously with the stress-assisted environmental rupture of the silica network. It is a fast procedure: typically at 0.5% strain in the aqueous sulphuric acid, the cracking occurs in 1.4 ~ 8.3 h [38]

However, some composite materials are quite resistant to the environmental attacks. The tests on the carbon-polyetheretherketone (PEEK) [40] showed that although the ultimate transverse strength lost 20% after 4.5 h of the water immersion, the stiffness of the material did not change even after 8 h of the water immersion.

Adams and Singh studied the effects of exposure to the hot, wet conditions on the mechanical properties of the carbon-epoxy and the carbon-PEEK. The carbon-PEEK was found to be little affected by the steam. For the carbon-epoxy, however, there was a decrease of about 13% in the apparent shear modulus when 2% moisture had been absorbed. The corresponding reduction in the interlaminar shear strength was 18% [41].

1.7.2 Diffusion

It is well-known that the moisture absorption in the presence of a humid environment is a basic physical property associated with the epoxy resins utilized in the composites, and the transportation of the moisture in the epoxy resin is a diffusion controlled process. The primary mechanism for the moisture absorption in the composite is by the instantaneous surface absorption and the subsequent diffusion through the material. The distribution of water or other solvents in a large flat sheet during the absorption or desorption is governed by the one-dimensional case of Fick's second law [42]:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right)$$

(9)
Where $t$ is the immersion time, $x$ is the space coordinate in direction of sheet thickness, $c$ is the concentration of diffusant, and $D$ is the diffusion coefficient.

The mass diffusivity $D$ depends on the temperature and the moisture as well. However, in most practical situations, the ambient temperature is uniform and $D$ changes little with the moisture content. Thus, we can simplify Equation 9 to:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

(10)

The solution to Equation 10 is given by Jost [43]:

$$c - c_s = 1 - \frac{4}{\pi} \sum_{j=1}^{\infty} \frac{1}{(2j+1)\pi} \sin \frac{\pi x}{h} \exp \left[ -\frac{(2j+1)^2 \pi^2 D t}{h^2} \right]$$

(11)

Where $h$ is the specimen thickness, $c_i$ is the initial moisture concentration in the specimen, and $c_s$ is the saturation moisture concentration in the specimen.

The total weight of the moisture in the material is obtained by integrating Equation 11 over the plate thickness. The result is:

$$\frac{M - M_i}{M_s - M_i} = 1 - \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{\exp[-(2j+1)^2 \pi^2 (Dt/h^2)]}{(2j+1)^2}$$

(12)

Where:

$$M = \frac{\text{Weight of specimen} - \text{Weight of dry specimen}}{\text{Weight of dry specimen}}$$
\[ \frac{M - M_i}{M_i - M_t} = \left( \frac{1}{\pi} \sqrt{\frac{D}{h^2}} \right)^{1/2} \quad \text{for } 0 \leq t < t_{0,u} \] (13)

\[ \frac{M - M_i}{M_i - M_t} = 1 - \frac{8}{\pi^2} \exp \left( -\pi^2 \frac{D t}{h^2} \right) \quad \text{for } t_{0,u} \leq t < \infty \] (14)

Where

\( t_{0,u} \) = the time required to reach 0.6M,

---

**Figure 1.9** Illustration of the change of moisture content with the square root of time \((M_m = M_t)\)
For a homogeneous wide plate, D can be calculated from Equation 13 and Figure 9:

\[
D = \pi \left( \frac{h}{4M_1} \right) \left( \frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \right)^2
\]

(15)

Where \(M_1\) and \(M_2\) are the moisture contents at the time \(t_1\) and \(t_2\). Equation 15 is widely used to calculate D value.

Non-Fickian absorption behaviour [33, 44, 45] in the composites has been reported as the results from both the chemical modification and the physical damage [3]. A crack mass-loss model was suggested by Zhou and Lucas [46]. Their results have show that the moisture related internal stress has a strong influence on D. By measuring the volume change of the polymer matrix under the moisture attack, Zhou and Lucas studied the stress-related cracks on the T300/934 carbon-epoxy composite material surface and then evaluated the relationship between the diffusion coefficient and the internal stress. They found for the samples after 4.3 kh immersion in 90°C water, the crack can be as deep as 0.5 mm. Thus, they believed the swell-related internal-stress and cracks was the key factor in the non-Fickian absorption study.

Gillat and Broutman studied the effect of external stress on the moisture diffusion in a carbon-epoxy system. Loading jig was used to apply stress on the diffusion samples. Diffusion coefficient was calculated and compared to the samples without external stress. They found D of the unstressed sample was 0.20 \(\mu\text{m}^2\text{s}^{-1}\), however, when 65% of ultimate
tensile strength was used, the diffusion coefficient became 1.16 \( \mu m^2 s^{-1} \), which was much higher than that of the unstressed sample [47].

Whitney and Browning realized that the internal stress played an important role in the diffusion process and they believed that the internal stress was the reason to many anomalies. Instead of a fixed \( D \), they used a stress dependent diffusion coefficient, and the stress changed with the time. Then this coefficient can be used in Fick’s law to evaluate the diffusion result [48].

### 1.8 Objective of This Study

The purpose of this study is to investigate the diffusion of hot water, acid and kerosene in the lab-made and the commercial polymeric composite systems including the carbon-epoxy, the carbon-polyimide and the glass-epoxy. In the first part of this study, we were trying to study the diffusion process on both the unidirectional and the cross-ply samples.

Also, this research was carried out to give more updated information of the environmental effects on the interlaminar strength, the fracture toughness and the transverse strength of those composite systems.
2 Experimental Method

2.1 Materials

Three kinds of fibre-polymer systems: carbon-epoxy, carbon-polyimide, and glass-epoxy, were used in the experiment. Prepregs were used to make the composites in the lab. The carbon-epoxy prepreg was T7G-145-F584-9, the carbon-polyimide prepreg was T9A-145-F655, which was a BMI resin based prepreg, and the glass-epoxy prepreg was T4S-216-F584. All three kinds of prepreg were obtained from Hexcel. To avoid the curing during the storage, all prepregs were kept in the cold room of −20°C. Data on these materials are given in table 2.1.

Table 2.1 Properties of the materials used

<table>
<thead>
<tr>
<th>Prepreg</th>
<th>Densities (kg/l)</th>
<th>Strength (GPa)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fibre</td>
<td>Matrix</td>
<td>Composite</td>
</tr>
<tr>
<td>Carbon-epoxy</td>
<td>1.77</td>
<td>1.22</td>
<td>1.54</td>
</tr>
<tr>
<td>Carbon-polyimide</td>
<td>1.77</td>
<td>1.25</td>
<td>-</td>
</tr>
<tr>
<td>Glass-epoxy</td>
<td>2.49</td>
<td>1.22</td>
<td>-</td>
</tr>
</tbody>
</table>

Fabricated unidirectional carbon-polyimide plates were also used in the experiments. Two kinds of fabricated carbon-polyimide plates were provided separately from Hexcel and NASA. The carbon-polyimide sample from Hexcel was T9A-145-F655-1, with a thickness of 2.14 mm. The sample from NASA was HL237, with a thickness of 3.15 mm.
2.2 Composite Fabrication

For the flat samples, the prepregs were cut into sheets with the desired size and the fibre direction and laid in a mould. The mould was made from steel and had dimensions of 250 x 250 mm. To make several composite panels at once, the aluminium sheets were used to separate the panels. The mould with cut prepreg inside was then put into a P-2150 hot-press, manufactured by PCI Inc. The mould was heated and put under the pressure. The curing process followed the profile recommended by Hexcel. That is, for the epoxy system, the condition was 2 hours under 180°C and for the polyimide system the condition was 7 hours under 240°C. The pressure for both systems was about 1.6 MPa.

For the “I.” shape samples used in the Curved Beam Strength (CBS) tests, a specially designed mould was used (see Figure 2.1). The curved beam consisted of two straight legs connected by a 90° bend with a 6.4 mm inner radius. The prepreg sheets can be laid and hot-pressed into a roof shape, and then be cut into the desired size.

Figure 2.1 Section of mould which was used for curved beam strength test
The inside of the hot-press moulds was sprayed with the PTFE release agent from Miller Stephenson Chemical Co. before the mould was assembled.

The dimensions of the specimens are shown in Figure 2.2. The specimens were cut to the approximate size with a diamond cutting wheel. To remove any potential small cracks, both edges of the specimens were polished using the #500 SiC-papers on a DAP-7 grinding machine, manufactured by Struers Inc.

![Figure 2.2 Front and top views of the curved beam strength sample](image)

The cross-ply samples were used for fracture toughness test and the unidirectional samples were used for the curved beam strength tests and the transverse strength tests. The environmental exposure tests were carried on both cross-ply and unidirectional sam-
2.3 Environmental Exposure

Three environments were used in the experiment. They are: water, kerosene and acid. For the water immersion, the water from the distilled water supply was used. The acid used in experiment was 20\% HCl (w/w). Both the cross-ply and the unidirectional samples were used. The size of the cross-ply samples was about 100mm x 25mm with a thickness of about 1.5 mm. The size of the unidirectional samples was about 100mm x 15mm with a thickness of about 2mm. The samples were weighed before and from time to time during the environmental exposure using a Gram-Atic balance, manufactured by E.METTLER Inc. Paper towel was used to remove the water from the sample surface before weighing. To ensure the precision of the exposure time measurement, the time for each weighing was kept under 15min. The water kerosene bath system is shown on Figure 2.3. A thermo controller was used to monitor and maintain the exposure temperature. For the acid exposure, room temperature was used and the samples were put into a sealed container in which the acid was held.
2.4 Composite Testing

2.4.1 Transverse Tensile Strength Testing

Specimens were cut to the approximate size with a diamond cutting wheel saw. To remove any potential cracks, both edges of the specimens were polished. The dimensions of the specimens are shown in Figure 2.4. The surfaces were prepared for end tabbing by lightly grinding using #120 SiC-paper. 2mm thick aluminium tabs with 20mm long and 15mm wide were ground using #120 SiC-paper and coated with LePage 12 epoxy glue. They were then held on the specimen ends using paper clamps. The samples were left at room temperature for curing for 24 hours.
Figure 2.4  Illustration of the transverse tensile strength test sample

The tests were performed on the Instron material test system (model 8800). The Instron machine grip force was reduced to the lowest limit to minimize the damage. The samples were directly mounted in the grips of the Instron machine and tensile load was applied using stroke control with a cross-head speed of 2 mm/min. The maximum load was recorded with the Dell computer.

2.4.2 Curved Beam Strength Testing

An out-of-plane (through the thickness) tensile stress is produced in the curved region of the specimen when load is applied with a four-point-bending test apparatus as shown in Figure 2.5 (ASTM D6415). Unidirectional specimens were used with the fibres running continuously along the legs and around the bend.
Figure 2.5 Illustration of four-point-bending test apparatus

The tests were performed on a 100 kN capacity Instron material test system (model 8800). The four-point-bending apparatus was mounted in the grips of the Instron machine. Then the samples were placed in the apparatus and a compressive load was applied using stroke control with a cross-head speed of 2mm min. The compressive load and the displacement were recorded with a Dell computer. The CBS were calculated using Equation 4 in the Introduction. ASTM D6415 suggests $D = 9.53\text{mm}$, $d_i = 12.5\text{mm}$, $\phi_i = 45^\circ$ and $t = 2\sim 12\text{mm}$. However, because of the environmental treatment, the modulus of samples are reduced and a large deformation was found. Thus, more vertical distance was required to give a result. To meet this requirement, the CBS tests were conducted with $D = 6.3\text{mm}$, $d_i = 10.3\text{mm}$, $\phi_i = 45^\circ$ and $t = 2.5\text{mm}$.
2.4.3 Fracture Toughness Testing

A notched sample was used in this test. After the flat composite plates were made by hot-pressing, they were cut into the desired size and shape (see Figure 2.6). A handsaw was used to obtain a proper notch width, which is about 0.5mm. The loading holes were drilled using a drill press. The tests were performed on the 100 kN capacity Instron material test system (model 8800). The pin loading clevises were mounted in the grips of the Instron machine. Then the samples were placed in the machine and the tensile load was applied using stroke control with a cross-head speed of 2mm/min. The maximum tensile loads were recorded using the Dell computer.

![Figure 2.6 Illustration of the translaminar fracture toughness test specimen and the test arrangement](image-url)
To obtain a consistent $K_{\text{RL}}$ measurement, a relatively small damage zone on the material is required. Thus, the typical load versus displacement plot should display relatively small amounts of displacement after the first drop. A criterion has to be followed to determine the maximum $K$ value using the maximum load value:

$$\frac{\Delta V_n}{V_{n_0}} \leq 0.3$$

where: $V_{n_0}$ and $\Delta V_n$ are defined in Figure 2.7.

![Diagram showing the criterion for $K_{\text{RL}}$ test on the load verse displacement plot.](image)

**Figure 2.7** Criterion for $K_{\text{RL}}$ test on the load verse displacement plot

### 2.5 Microscope Examination

Fracture surfaces were examined in a HITACHI scanning electron microscope. In addition, the samples were sectioned at right angle to the fibres and the sections were polished. The section were then examined under Olympus universal research microscope Model VANOX at X 330, and the images were scanned and recorded using a Macintosh computer.
3 Experimental Results

3.1 Moisture Absorption

3.1.1 Unidirectional Samples

Figures 3.1 ~ 3.4 show the curves of the weight-gain of the unidirectional carbon-epoxy and the carbon-polyimide samples in 60°C and 90°C water which plotted vs. square root of time.

Figure 3.1 shows the carbon-epoxy in 90°C and 60°C water. For 90°C samples, the absorption curve had two linear regions, the first was to about 150 h and the second was up to 2500 h. The sample reached the saturation of about 2% after about 3 kh immersion. For the samples in 60°C water, the absorption rate changed several times. The rate increased continuously during the first 400 hours. After that, at a weight gain of 0.8%, the rate decreased slightly but with no indication of the saturation.

Figure 3.2 shows that of the carbon-polyimide fabricated by Hexcel in 90°C and 60°C water. Rapid linear absorption was observed at the beginning up to about 120 h in the 90°C samples. Then the absorption slowed down at 125 h to give another approximately straight line which extended until 2 kh was reached. By then, the absorption process reached its saturation, which was about 0.6%. For the 60°C samples, a rate increase was found during the initial several hours, followed by a linear region. The absorption rate then went down and another linear region was observed. This change occurred after 0.25 kh of immersion. The absorption rate of 90°C samples was higher than that of 60°C samples, but had lower saturation moisture content.
Figure 3.1  Moisture absorption of carbon-epoxy in 90°C and 60°C water

Figure 3.2  Moisture absorption of carbon-polyimide fabricated by Hexcel in the 90°C and 60°C water
Figure 3.3 shows the moisture absorption curves of the carbon-polyimide fabricated by NASA in the 90°C and 60°C water. In the first several hours, the absorption rate of the 90°C samples was low, then it rose and became linear until the sample weight increased by 0.3%. When the curve was approaching the saturation, it still gave a slightly increasing line. A rate increase in the 60°C sample was found during the initial hours, followed by a linear region. The absorption rate then went down and another linear region was observed at 0.4 kh. The initial absorption rate of 90°C samples was higher than that of the 60°C samples, but had lower second absorption rate.

Figure 3.4 shows that for the lab-made carbon-polyimide in 90°C and 60°C water. The initial absorption rate of the 90°C specimen was very rapid. After about 60 h, the rate decreased and then increased again to give a straight line. The saturation was observed after about 2 kh at a weight gain of about 3%. Compared with that of 90°C, the absorption of the 60°C specimen was almost the same except that it did not reach the saturation point even after 5 kh of immersion.

3.1.2 Cross-ply Samples

Figures 3.5 showed the weight-gain vs. square root time plot of the cross-ply carbon-epoxy in 60°C and 90°C water. In both cases, after an initial linear slope, the absorption rate dropped to a lower linear rate until the saturation was reached. For the carbon-epoxy in the 90°C water (see Figure 3.5), the rate change happened after 60 hours of immersion and the weight loss was observed after the saturation point. For the 60°C carbon-epoxy samples, the rate change occurred after 0.4 kh of immersion.
Figure 3.3  Moisture absorption of the carbon-polyimide fabricated by NASA in 90°C and 60°C water

Figure 3.4  Moisture absorption of the lab-made carbon-polyimide in 90°C and 60°C water
Figure 3.5 Moisture absorption of the cross-ply carbon-epoxy in 90°C and 60°C water

Figure 3.6 Moisture absorption of the cross-ply lab-made carbon-polyimide in 90°C and 60°C water
Figure 3.6 shows the comparison of the absorption behaviour of the lab-made carbon-polyimide in 90°C and 60°C water. Significant absorption rate change was also observed in both cases after 0.1 kh of immersion. There was only slight difference between the absorption rates of the 90°C and the 60°C systems. However, after about 3 kh of immersion, the 90°C samples reached the saturation but the absorption of the 60°C specimen was continuous.

### 3.1.3 Absorption in Strong Acid and Kerosene

Figures 3.7–3.11 show the weight-gain vs. square root time plot of the glass-epoxy, the carbon-epoxy and the carbon-polyimide in the 80°C kerosene and the room temperature 20% HCl acid. For the glass-epoxy and the carbon-epoxy samples in the room temperature acid, the weight-gain can be as high as 14% (see Figures 3.7 and 3.8). However, the carbon-polyimide sample show good acid resistance and the saturation moisture content was only about 1.3% in 20% HCl (see Figure 3.9). The 80°C kerosene has no significant effect on both the carbon-epoxy and the carbon-polyimide. The saturation contents of samples in kerosene were very low.

Low weight gain amount was observed in the carbon-polyimide samples. See Figure 3.9. The saturation was reached after about 1.5 kh of immersion. 2-stage absorption was also observed.

The carbon-epoxy (Figure 3.10) showed unique absorption behaviour in the kerosene. It did not gain weight until after about 8 kh of immersion. Then the 2-stage absorption was observed. The absorption rate change occurred after about 2.5 kh of immersion and the process did not reach the saturation after 7 kh of immersion.
Figure 3.7 Moisture absorption of the cross-ply glass-epoxy in the 20% HCl

Figure 3.8 Moisture absorption of the cross-ply carbon-epoxy in the 20% HCl
Figure 3.9 Moisture absorption of the lab-made cross-ply carbon-polyimide in the 20% HCl

Figure 3.10 Absorption of the cross-ply carbon-epoxy in the 80°C kerosene
Figure 3.11 shows the absorption curves of the cross-ply carbon-polyimide in the 80°C kerosene. Small weight gain was observed.

3.2 Transverse Strength

Figure 3.12 shows the typical carbon-epoxy force-displacement curves at the different stages of the transverse strength test. It includes a linear increasing part followed by a sudden drop. Thereafter on the 0 h curves and on the 60°C 4 h curve there was some small increase of force and it was found that there were fibres across the crack planes. The force-displacement slopes of the 60°C samples are almost the same, but the angles of the slopes of the 90°C samples decreased with increasing immersion time. For both the 60°C and the 90°C systems, the maximum force decreased with the increasing of the immersion time.
The moisture effect on the transverse strength of the carbon-epoxy is illustrated in Figure 3.13. Slight strength loss (about 20%) was observed.

Figure 3.14 shows the effect of the 60°C and the 90°C water immersion on the transverse modulus of the carbon-epoxy. For the 90°C samples the modulus decreased and for the 60°C samples the modulus was unchanged.

![Typical force-displacement curves of the carbon-epoxy transverse strength tests](image)

**Figure 3.12** Typical force-displacement curves of the carbon-epoxy transverse strength tests: (a) in the 60°C water; (b) in the 90°C water
Figure 3.13  Effect of 60°C and 90°C water immersion on the transverse strength of the carbon-epoxy

Figure 3.14  Effect of 60°C and 90°C water immersion on the transverse modulus of the carbon-epoxy
Figure 3.15 shows the typical Hexcel carbon-polyimide force-displacement curves at the different stages of the transverse strength test in the 60°C and the 90°C water. There was some small increase of force thereafter on the 0 kh curve, which indicated some fibre-bridges on crack planes. However, such a phenomena was not observed on treated samples. After 4 kh of immersion, the strength of both the 60°C and the 90°C samples dropped by about 40%.

Figure 3.16 shows the effect of the 60°C and the 90°C water immersion on the transverse strength of the Hexcel carbon-polyimide. The strength of both samples decreased about 25%. Figure 3.17 shows the effect on the transverse modulus. The modulus of the 90°C samples decreased by nearly 70% while at 60°C the modulus stayed about the same.

Figure 3.15  Typical force-displacement curves of the Hexcel carbon-polyimide transverse strength tests: (a) in the 60°C water; (b) in the 90°C water
Figure 3.16 Effect of the 60°C and the 90°C water immersion on the transverse strength of the Hexcel carbon-polyimide

Figure 3.17 Effect of the 60°C and the 90°C water immersion on the transverse modulus of the Hexcel carbon-polyimide
Figure 3.18 shows the typical NASA carbon-polyimide force-displacement curve at the different stages of transverse strength test in the 60°C and the 90°C water. An increase in breaking force was found on the 0 kh and the 2 kh samples in both environments. The increasing forces of the NASA samples are as high as about 20% of the maximum force and are greater than with the other composite materials. The water immersion only changed the maximum force slightly even after 4 kh of immersion.

Figure 3.19 shows the effect of 60°C and 90°C water immersion on the transverse strength of the NASA carbon-polyimide. The strength of the NASA samples virtually remained unchanged. Figure 3.20 shows the effect on the transverse modulus. No significant change was observed.

Figure 3.18  Typical force-displacement curves of the NASA carbon-polyimide transverse strength tests: (a) in the 60°C water; (b) in the 90°C water
Figure 3.19  Effect of the 60°C and the 90°C water immersion on transverse strength of NASA carbon-polyimide

Figure 3.20  Effect of the 60°C and the 90°C water immersion on the transverse modulus of the NASA carbon-polyimide
Figure 3.21 showed the typical force-displacement plots of the lab-made carbon-polyimide. The water immersion decreased the maximum force in both systems. The 90°C samples lost about 50% of the strength after 2kh immersion and the 60°C samples lost about 20%. Fibre bridging was observed on both the 60°C and the 90°C 4 kh samples. Figure 3.22 shows the effect of the 60°C and the 90°C water immersion on the transverse strength of the lab-made carbon-polyimide. The strength of all samples dropped after the immersion. The 90°C samples losing more strength than the 60°C samples. Figure 3.23 shows the effect on the transverse modulus. The modulus of 90°C samples decreased by more than 50%.

![Figure 3.21](image)

**Figure 3.21** Typical force-displacement curves of the lab-made carbon-polyimide transverse strength tests: (a) in the 60°C water; (b) in the 90°C water
Figure 3.22  Effect of the 60°C and the 90°C water immersion on the transverse strength of the lab-made carbon-polyimide

Figure 3.23  Effect of the 60°C and the 90°C water immersion on the transverse modulus of the lab-made carbon-polyimide
As we can find in the charts above, all force-displacement plots are curves instead of lines. Table 3.1 shows the ratios of the inelastic/elastic deformation on the $\sigma_{20}$ tests. This ratio was obtained by extrapolating the initial slope to the maximum force, and taking the ratio of the actual failure displacement to this elastic displacement.

| Table 3.1 Ratio of the inelastic/elastic deformation on the $\sigma_{20}$ tests |
|---------------------------------|-----------------|---------------|-----------------|-----------------|
|                                 | 60°C water      | 90°C water    |                 |                 |
|                                 | 0 kh            | 2 kh          | 4 kh            | 2 kh            | 4 kh            |
| Carbon-epoxy                    | 0.18±0.04       | 0.13±0.02     | 0.14±0.09       | 0.09±0.09       | 0.13±0.03       |
| Hexcel                           | 0.11±0.03       | 0.10±0.02     | 0.07±0.05       | 0.07±0.04       | 0.14±0.03       |
| NASA                             | 0.24±0.03       | 0.34±0.07     | 0.22±0.08       | 0.18±0.07       | 0.13±0.06       |
| Lab-made                         | 0.14±0.02       | 0.19±0.16     | 0.09±0.03       | 0.06±0.03       | 0.11±0.04       |

Note: 1, 2 and 3 are carbon-polyimide systems

### 3.3 Curved Beam Strength

Figure 3.24 shows typical force-displacement curves of the carbon-epoxy CBS tests in the 60°C water and in the 90°C water. The maximum force and the maximum displacement of the 90°C samples dropped significantly with the immersion time (by about 50% at 2 kh and 75% at 4 kh). The maximum force of 60°C samples decreased slightly, while the maximum displacement decreased by 30% at 2 kh and 50% at 4 kh. Figure 3.25 shows the effect of the 60°C and the 90°C water immersion on the CBS of the Carbon-Epoxy. The CBS of the 60°C samples increased by almost 100% and that of the 90°C samples dropped by half.

Figure 3.26 shows the typical force-displacement curves of the carbon-epoxy CBS tests in oil and in the HCl. The ratios of the force/displacement increased with increasing of immersion time. For the samples immersed in paraffin oil at 80°C, the maximum force decreased by about 40% at 2 kh and 4 kh, and the samples immersed for 2 kh had a double peak. For the HCl samples, the maximum force dropped by about 40% at 2 kh and 70% at 4 kh. There was also very considerable force recovery in the 4 kh case.
Figure 3.27 shows the effect of the paraffin oil and the HCl immersion on the CBS of carbon-Epoxy. The HCl reduced the CBS by 20% and the oil increased the CBS by 100%.

**Figure 3.24** Typical force-displacement curves of the carbon-epoxy CBS tests: (a) in the 60°C water; (b) in the 90°C water

**Figure 3.25** Effect of the 60°C and the 90°C water immersion on the CBS of the carbon-epoxy
Figure 3.26  Typical force-displacement curves of the carbon-epoxy CBS tests: (a) in the oil; (b) in the HCl

Figure 3.27  Effect of the oil and the HCl immersion on the CBS of the carbon-epoxy
Figure 3.28 shows typical force-displacement curves of the lab-made carbon-polyimide CBS tests in the 60°C and the 90°C water. The ratios of force/displacement were about the same for all samples. The maximum force of the 60°C samples dropped by about 60% at 2 kh and about 50% at 4 kh. For the 90°C water samples, the decrease was about 70% for both 2 kh and 4 kh. Figure 3.29 shows effect of the 60°C and the 90°C water immersion on the CBS of the lab-made carbon-polyimide. The 60°C water increased its CBS by about 50% and the 90°C water had no significant effect on the samples.

Figure 3.30 shows typical force-displacement curves of the lab-made carbon-polyimide CBS tests in the oil and the HCl. The ratios of force/displacement increased with the increasing of the immersion time. The maximum force of the oil samples dropped by about 50% and 20% at 2 kh and 4 kh respectively. For the HCl samples, they are about 20% and 30% at 2 kh and 4 kh respectively. Figure 3.31 shows the effect of the oil and the HCl immersion on the CBS of the lab-made carbon-polyimide. A very large CBS increase (about 150%) was observed.

![Figure 3.28](image-url)  
**Figure 3.28** Typical force-displacement curves of the lab-made carbon-polyimide CBS tests: (a) in the 60°C water; (b) in the 90°C water
Figure 3.29  Effect of the 60°C and the 90°C water immersion on the CBS of the carbon-polyimide

Figure 3.30  Typical force-displacement curves of the lab-made carbon-polyimide CBS tests: (a) in the oil; (b) in the HCl
Figure 3.31 Effect of the oil and the HCl immersion on the CBS of the lab-made carbon-polyimide

Table 3.2 showed the ratio of the maximum force / displacement on the CBS tests.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>0 kh</th>
<th>2 kh</th>
<th>4 kh</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Carbon-epoxy</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60°C water</td>
<td></td>
<td>0.50±0.05</td>
<td>0.69±0.09</td>
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</tr>
<tr>
<td>90°C water</td>
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<td>0.36±0.04</td>
<td>0.2±0.1</td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td></td>
<td>0.28±0.07</td>
<td>0.51±0.03</td>
<td></td>
</tr>
<tr>
<td>Oil</td>
<td></td>
<td>0.54±0.06</td>
<td>0.58±0.07</td>
<td></td>
</tr>
<tr>
<td><strong>Carbon-polyimide</strong></td>
<td></td>
<td>0.18±0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60°C water</td>
<td></td>
<td>0.54±0.04</td>
<td>0.53±0.07</td>
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</tr>
<tr>
<td>90°C water</td>
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<td>0.45±0.07</td>
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</tr>
<tr>
<td>HCl</td>
<td></td>
<td>0.64±0.04</td>
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<td></td>
</tr>
<tr>
<td>Oil</td>
<td></td>
<td>0.5±0.1</td>
<td>0.77±0.01</td>
<td></td>
</tr>
</tbody>
</table>
3.4 Fracture Toughness

Figure 3.32 shows typical force-displacement curves of the carbon-epoxy fracture toughness tests in the 60°C and the 90°C water. The 60°C water had no significant effect on the samples up to 2 kh. However, the maximum force dropped by about 30% at 4 kh. The 90°C water decreased the maximum force by about 15% at 2 kh and 30% at 4 kh. In both environments, the 2 kh samples had a large drop after the maximum force compared with the other samples. Figure 3.33 shows the effect of the 90°C and the 60°C water immersion on the $K_{TL}$ of the carbon-epoxy. In both cases $K_{TL}$ was approximately constant up to about 5 kh and then significantly decreased.

![Typical force-displacement curves](image)

**Figure 3.32** Typical force-displacement curves of the carbon-epoxy Fracture Toughness tests: (a) in the 60°C water; (b) in the 90°C water
Figure 3.33 Effect of the 90°C and the 60°C water immersion on the $K_{\text{TL}}$ of the carbon-epoxy

Figure 3.34 shows typical force-displacement curves of the carbon-epoxy fracture toughness tests in the HCI and in the oil. The 20% HCl acid decreased the maximum force by about 40% and 60% at 2 kh and 4 kh respectively. The maximum force of the paraffin oil sample didn't change very greatly at the first 2 kh (by about 15%). At 4 kh, however, the sample lost about 50% of its strength. Figure 3.35 shows the effect of the paraffin oil and the HCl immersion on the $K_{\text{TL}}$ of the carbon-epoxy. Slight decreases were found in both the oil and the HCl samples. However, the change occurred only after 6 kh to the paraffin oil samples while it took the HCl only 1 kh to change $K_{\text{TL}}$.

Figure 3.36 shows typical force-displacement curves of the lab-made carbon-polyimide fracture toughness tests in the 60°C and the 90°C water. The effects of the 60°C water on the samples were not very large. There was no noticeable change after 2 kh of immersion and the maximum force dropped by about 20% after 4 kh of immersion. The 90°C water had slight effect on the samples, the maximum force decreased by about
15% and 30% at 2 kh and 4 kh respectively. Figure 3.37 illustrates the effect of the 90°C and the 60°C water immersion on the $K_{TL}$ of the lab-made carbon-polyimide. The fracture toughness dropped slightly and there was no significant difference between the 60°C and the 90°C samples.

![Figure 3.34](image)

**Figure 3.34** Typical force-displacement curves of the carbon-epoxy Fracture Toughness tests: (a) in the HCl, and (b) in the oil

![Figure 3.35](image)

**Figure 3.35** Effect of the oil and the HCl immersion on the $K_{TL}$ of the carbon-epoxy
Figure 3.36  Typical force-displacement curves of the lab-made carbon-polyimide Fracture Toughness tests: (a) in the 60°C water; (b) in the 90°C water.

Figure 3.37  Effect of the 90°C and the 60°C water immersion on the $K_{TI}$ of the lab-made carbon-polyimide
Figure 3.38 shows the effect of the paraffin oil and the HCl immersion on the typical force-displacement curves of the lab-made carbon-polyimide. The acid reduced the maximum force by about 10% and 25% at 2 kh and 4 kh respectively. The oil, however, has no significant effect on the samples. The Figure 3.39 shows the effects on the $K_{\text{TI}}$. A slight decrease was observed in the tests.

Figure 3.40 shows the effect of the HCl immersion on the typical force-displacement curves of the glass-epoxy. The acid reduced the maximum force by about 50% after 2 kh of immersion and there is no further force lost after that. The acid also reduced the ratio of force/displacement significantly. The effects of the acid on the $K_{\text{II}}$ is shown in Figure 3.41. The HCl did significant damage to the samples and the $K_{\text{II}}$ dropped by 50% before the first 1 kh of immersion.

![Figure 3.38](image1)

![Figure 3.40](image2)

**Figure 3.38** Typical force-displacement curves of the lab-made carbon-polyimide Fracture Toughness tests: (a) in the HCl, and (b) in the oil.
Figure 3.39  Effect of the oil and the HCl immersion on the $K_{IL}$ of the lab-made carbon-polyimide.

Figure 3.40  Typical force-displacement curve of the glass-epoxy Fracture Toughness tests in the HCl.
Figure 3.41  Effect of HCl immersion on $K_{11}$ of glass-epoxy

Table 3.3 shows the ratio of the displacement at 20% of the maximum force to displacement at the maximum force in the $K_{11}$ tests.

Table 3.3 Ratio of (the displacement at 20% of the maximum force after failure / displacement at the maximum force) in the $K_{11}$ tests

<table>
<thead>
<tr>
<th></th>
<th>0 kh</th>
<th>2 kh</th>
<th>4 kh</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Carbon-epoxy</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60°C water</td>
<td>1.4±0.1</td>
<td>1.6±0.2</td>
<td>1.6±0.3</td>
</tr>
<tr>
<td>90°C water</td>
<td>1.3±0.1</td>
<td>1.9±0.1</td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td>1.3±0.1</td>
<td>1.4±0.3</td>
<td></td>
</tr>
<tr>
<td>Oil</td>
<td>1.3±0.1</td>
<td>1.4±0.2</td>
<td></td>
</tr>
<tr>
<td><strong>Carbon-polyimide</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60°C water</td>
<td>1.3±0.3</td>
<td>1.2±0.1</td>
<td></td>
</tr>
<tr>
<td>90°C water</td>
<td>1.2±0.4</td>
<td>1.5±0.3</td>
<td></td>
</tr>
<tr>
<td>HCl</td>
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<td>1.8±0.1</td>
<td></td>
</tr>
<tr>
<td>Oil</td>
<td>1.1±0.1</td>
<td>1.2±0.2</td>
<td></td>
</tr>
</tbody>
</table>

3.5  Image Analysis

3.5.1  SEM Observations

Figures 3.42–3.47 show the scanning electron microscopic pictures taken from the fracture surface of the samples. Figures 3.43 and 3.44, which compare the carbon-
carbon-epoxy transverse fracture surface before and after the immersion, show very little change. Much polymer can be seen adhering to the fibre.

The transverse fracture surface of the Hexcel moulded carbon-polyimide showed a moderate amount of the bare fibre (see Figure 3.44). However, after immersion much less polymer was seen to be adhering to the fibre (see Figure 3.45).
Figure 3.44  Transverse fracture surface of the untreated Hexcel carbon-polyimide sample

Figure 3.45  Transverse fracture surface of the Hexcel carbon-polyimide sample after 2.5 hr in the 90°C water

The NASA carbon-polyimide transverse fracture surface showed almost no polymers adhering to the fibre (see Figure 3.46). There is even less after 2.5 hr im-
But the water immersion did not appear to affect it.

Figure 3.46 Transverse fracture surface of the untreated NASA carbon-polyimide sample

Figure 3.47 Transverse fracture surface of the NASA carbon-polyimide sample after 2.5 kh in the 90°C water

3.5.2 Fibre Volume Fractions

Figure 3.48 shows light microscope pictures of cross-sections of the unidirectional samples. The carbon fibres in the lab-made carbon-polyimide composite ma-
terial are thicker than the other samples. The NASA samples, on the other hand, have finer carbon fibres. Also, the NASA sample has even fibre distribution than the other samples.

Figure 3.48 Cross-intersection images (X330) of: (a) the lab-made carbon-epoxy; (b) the lab-made carbon-polyimide; (c) the Hexcel carbon-polyimide and (d) the NASA carbon-polyimide

The scanned images of sections of the composites were processed to the yield fibre volume fractions, with the results as follows, for the unidirectional samples.

Table 3.4 Fibre volume fractions and densities of the unidirectional samples

<table>
<thead>
<tr>
<th>System</th>
<th>Fibre volume fraction</th>
<th>Density (Mgm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon-epoxy</td>
<td>Lab-made</td>
<td>63.4±0.2</td>
</tr>
<tr>
<td>Carbon-polyimide</td>
<td>Hexcel¹</td>
<td>50.0±0.1</td>
</tr>
<tr>
<td></td>
<td>NASA²</td>
<td>43.4±0.5</td>
</tr>
<tr>
<td></td>
<td>Lab-made²</td>
<td>54.2±0.8</td>
</tr>
</tbody>
</table>

Note: ¹ and ² were moulded by Hexcel and NASA respectively. ³ was moulded in laboratory
4 Discussion

4.1 Fluid Absorption

The experimental results showed that diffusion processes in our tests are slow. For the lab-made unidirectional carbon-epoxy composites immersed in the 90°C water, the saturation was reached after 3 kh of immersion. The lab-made cross-ply carbon-epoxy immersed in the 60°C water was not saturated even after 6 kh of immersion. Also, it appeared that the maximum moisture content is different at different temperatures.

The carbon-polyimide commercial samples, which were unidirectional, obeyed Fick's law well at 90°C (see Figure 3.2 and 3.3), with $M_s = 0.59\%$ for the Hexcel sample, and a little less for the NASA sample. D values were respectively about 1.3 and 0.7 $\mu$m$^2$/s. However, they did not have purely Fickian behaviour at 60°C: there was some evidence of a second linear region in the plots after about 0.6 kh in both cases. If we ignore this and assume that saturation was reached after about 4 kh, we have lower values for $M_s$ of 0.68% for the Hexcel sample and 0.55% for the NASA sample, i.e. a little bit less than at 90°C in both cases.

The D values were respectively about 0.48 and 0.25 $\mu$m$^2$/s. These values were estimated by finding the intersection of the extrapolated initial linear region, and the line representing $M_s$; see Figure 4.1, which shows the construction. If $(t_s, M_s)$ are the coordinates of the intersection point, it can easily be shown that the Equation 15 reduces to:

$$D = \pi h^2 / 16 t_s$$  \hspace{1cm} (16)

This method allows us to extract data from some of the other plots, which do not obey Fick’s law. For example, in the case of the samples which appeared to display linear
regions in the M vs. $\sqrt{t}$ plot, such as shown for the example in Figure 3.1 for the carbon-epoxy at 90°C, we can suppose that stage 1 of the absorption involves a saturation value of about 1.4%, since Fick’s law can be fitted reasonably well to this with a diffusive constant $D_1$ of 0.41 mm$^2$/s (see Figure 4.2). Stage 2 of the absorption is assumed to start at $M_{d1}$ and continue to $M_{d2}$ which appears to be the overall maximum water absorption indicated in Figure 4.2. We further assume that for the second stage, the saturation value is $M_{d2} = M_{d3} - M_{d1}$, and that we can estimate the effective diffusion rate $D_2$ from the intersections $t_{d1}$ and $t_{d2}$, assuming we can use equation 13 with $t_{d2} = t_{d1} - t_{d1}$. Thus we obtain, for stage 2, $M_{d2} = 0.7\%$ and $D_2 = 0.13 \mu m^2/s$.

The carbon-epoxy cross ply absorption at 90°C can be treated in the same way, if we ignore the dissolution that is occurring after about 2 kh. Taking $M_{d1}$ as 0.2% gives $D_1$ 1.32 mm$^2$/s, and with $M_{d2}$ taken as 0.2%, $D_2$ comes to about 0.12 mm$^2$/s. Thus in stage 1 the cross ply appears to absorb slightly less water but at a much faster rate, while in stage 2 it absorbs much less water, at about the same rate. After 2 kh, the dissolution is roughly linear with time. Assuming that is also occurring at the start of the water absorption, the effect would be small at $t_{d1}$ (93h), since the rate is approximately 0.05% per 1 kh. However, it could increase $M_i$ from 0.2 to 0.3%, but this still leaves it much less than the value for the unidirectional case.
Figure 4.1 An absorption curve with constant diffusivity (NASA unidirectional Carbon-Polyimide sample in 90°C water)

Figure 4.2 A 2-stage absorption curve (unidirectional carbon-epoxy in 90°C water)

The unidirectional and cross ply carbon-epoxy samples did not show any signs of reaching equilibrium water content at 60°C, even after 4 h and 6 h immersion respectively. Previous work [48] with epoxies showed that the water solubility was approximately constant when the temperature was varied. Thus for Dow DER 332 resin, without fibre present, $M_s$ increased from about 2.7% at 22°C to about 2.9% at 100°C. (However, our results showed that the carbon-polyimide samples investigated here did
not obey $M_i = \text{constant}$ as well as this: absorption decreased between 60°C and 90°C by about 13% in both cases). Strict adherence to $M_i = \text{constant}$ would provide an estimate of the $D_1$ value at 60°C, $D_1(60)$, since the slopes, $m_1(60)$ and $m_1(90)$, of the initial part of the absorption curves would then be in direct proportion to the square roots of the diffusion coefficients:

$$\frac{D_1(90)}{D_1(60)} \equiv \left( \frac{m_1(90)}{m_1(60)} \right)^2$$  \hspace{1cm} (17)

this gives very approximate $D_1$ values of 0.1$\mu$m$^2$/s for the unidirectional and 0.27$\mu$m$^2$/s for the cross-ply samples.

Extra confidence in these estimates comes from the Arrhenius equation:

$$D = D_0 \exp(-E_d/RT)$$  \hspace{1cm} (18)

Where $D_0$ is a constant. $E_d$ is the activation energy for diffusion. $R$ is the gas constant (8.31 JK$^{-1}$mol$^{-1}$) and $T$ is the temperature, K. This reduces to

$$E_d \approx 36 \ln \frac{D_1(90)}{D_1(60)} \text{ kJ/mol}$$  \hspace{1cm} (19)

While give $E_d$ values of 26 kJ/mol for the unidirectional and 29 kJ/mol for the cross-ply cases. These are not unreasonable compared with the previous work [48], where values of 48 and 41 kJ/mol were observed for epoxies.

Applying the same analysis to the second region gives 0.002 and 0.011 $\mu$m$^2$/s for the unidirectional and cross ply cases respectively. All the above results are listed in Table 4.1.

The results shown in Table 4.1 indicate that the NASA polyimide is more resistant to water than the Hexcel polyimide. It absorbs less and the water diffuses more
slowly. Based on a fibre volume fraction $V_f$ of 0.43, the polymer would absorb about 0.84% of water at 90°C, compared with 1.14% for the Hexcel polyimide. PEEK is more resistant than this, with $M_{sp} = 0.52\%$, but with $D_I = 11.2 \mu m^2 s$ [40]. For the NASA samples, we estimate $D_p$, the diffusion coefficient for the polymer, using previous work [49] which indicated that for $V_f = 0.4$, $D/I = 0.5$, hence $D_p = 1.42 \mu m^2 s$.

The $M_{sp}$ values of unidirectional carbon-epoxy are similar to the earlier epoxy results [48]. Here we estimate $M_{sp} = 4\%$, as compared with about 3\%, but with $D_p$, somewhat less, i.e. 1.0 compared with 6.1$\mu m^2/s$.

<table>
<thead>
<tr>
<th>Table 4.1 Diffusion data estimated from the water absorption plot</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>System</strong></td>
</tr>
<tr>
<td>-------------</td>
</tr>
<tr>
<td>Carbon-epoxy</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Carbon-polyimide</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

Note: 1 and 2 moulded respectively by Hexcel and NASA. 3 moulded in the laboratory.

The lab-made carbon polyimide laminate had a higher $M_I$ and much higher $D_I$ than the Hexcel made laminate. The volume fraction of matrix could be playing a role here, and also possible voids. Although voids could not be seen in the images of the polished section, we can estimate the void content from densities, $\rho_v$, of the composites. since:

\[ \rho_v = V^i \rho_v + V^m \rho_m \]

(20)

Also, since:
\[ V_f + V_m + V_v = 1.0 \]  \hspace{1cm} (21)

We can substitute equation 21 into equation 20, and re-arrange to give:

\[ V_v = 1 - V_f - (\rho_v - \rho_f) / \rho_m \]  \hspace{1cm} (22)

Here subscripts \( f \) and \( m \) are for fibres and matrix as before, and \( v \) is for voids.

Substituting values for \( \rho_f \) and \( \rho_m \) from Table 2.1 and \( \rho_v \), \( V_f \) from Table 3.1, we find that the Hexcel laminate had about 2\% voids and the lab-made laminate about 6\%. This indicates that in the lab we could not achieve the quality of laminate expected commercially. The fibre volume fraction was also lower. Thus the pressure applied (1.6 MPa) was not so effective in our lab, so that less polymer was squeezed out. Moreover, the water produced in the curing action was probably not so well eliminated either, giving rise to the higher void content. These weaknesses, however, may be used to determine the effects of voids on water absorption.

At the first apparent saturation, \( M_{\text{sat}} \), we will assume that the polymer is saturated, with water content \( M_{wp} \). The voids contain the remainder of the water, \( M_v \), but are not necessarily saturated. We assume that the amount of water in the fibres and at the fibre-matrix interface is negligible. Thus:

\[ M_{\text{sat}} = V_m M_{wp} + V_v M_v \]  \hspace{1cm} (23)

Using our values of \( M_{\text{sat}} \) for the Hexcel and lab-made carbon-polyimide, \( V_m \) estimated from Table 3.1 using equation 21, together with value of \( V_v \) (2\% and 6\%) just derived, we have two simultaneous equation derived from equation 23. These give \( M_{wp} = 1.4\% \) at 60\(^\circ\)C and 1.1\% at 90\(^\circ\)C. The corresponding value of \( M_v \) are 3\% and 4\%.

Thus, proportionately more water resides in the voids.
Next we can check whether the voids filled up with water vapour at the pressure expected for water in equilibrium. At 60°C this is 19.9 kPa and at 90°C this is 70.1 kPa [50]. Let this be \( P_a \). We can calculate the amount of water, this involves from the Gas Law, \( PV=nRT \). Thus:

\[
n_a = \frac{P_a V_a}{RT}
\]

(24)

If we consider one cubic meter of composite, \( V_{a1} = 0.02 \, \text{m}^3 \) for the Hexcel laminate and 0.06 m³ for the lab made one. Since water has a molecular weight of 18, then the amount of water per cubic meter, \( M_a \), in the voids is:

\[
M_a = 18 P_a V_a / RT
\]

(25)

with \( M_a \) in grams per cubic meter of composite.

Using equation 25 gives the maximum values 7.93g/l for the Hexcel composite and 23.8g/l for the lab made at 90°C, and the corresponding value at 60°C are 2.25g/l and 6.75g/l. Dividing by the densities (in g/cc) and dividing by 10 gives the maximum \( M_i \) in %.

Finally, substituting these values into equation 23 with known \( M_{a1}, V_m, M_{a2}, \) and \( V \), gives a theoretical maximum absorbed, i.e., \( M_{a2} \), see Table 4.2.

<table>
<thead>
<tr>
<th>System</th>
<th>60°C</th>
<th>Theory (%)</th>
<th>90°C</th>
<th>Theory (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexcel</td>
<td>0.68</td>
<td>0.77</td>
<td>0.57</td>
<td>1.00</td>
</tr>
<tr>
<td>Lab-made</td>
<td>&gt;2.6</td>
<td>1.21</td>
<td>2.8</td>
<td>2.27</td>
</tr>
</tbody>
</table>

Table 4.2 Theory vs. experiment for voids filling with water

The table clearly demonstrates that void filling is not the mechanism involved. Thus, the Hexcel composite has \( M_{a2} = 0 \), so the theoretical values is much higher than the experimental result. Moreover, the lab made composite has a theoretical result less than the experimental. It seems much more likely therefore that the water damages the lab
made composite. The voids in this case were probably areas of imperfect lamination. Water could enter these and create osmotic pressure as a result of dissolution of uncured resin components present there. It concluded therefore that the results support the cracking mechanism described by Zhou and Lucas [46].

When the glass epoxy and carbon epoxy samples were immersed in 20% HCl, the acid must have reacted with the resin, to give the consistently high M₄ values observed, i.e., 14% and 12% respectively. There may have been a little reaction with the glass as well, since the glass value was higher, see Figure 3.7. The HCl appears to have been less reactive with the polyimide than water alone, since in this case, M₄₁=M₄₃=1.24, compared with M₃₁=1.74 for 90°C water for the cross ply case (compares Figures 3.9 & 3.6).

Neither the carbon-epoxy nor the carbon-polyimide was much affected in kerosene: see Figures 3.10 & 3.11.

### 4.2 Transverse Strength

All the laminates tested failed suddenly and more or less completely, whether water treated or not, see Figures 3.12, 3.15 and 3.18. In the rare cases of a slight recovery after failure, this was due to fibers, probably slightly misaligned, crossing the crack plane. Nearly all the force-distance plots were curves, and the degree of deviation from linearity for each case are given in Table 3.1. These values are the ratios of the strains at failure / the strain at failure estimated from the slope near the origin. Water immersion generally reduced this "ductility". However, both Hexcel molded and lab molded carbon-polyimide showed some recovery after 4kh at 90°C. This was accompanied by a very large reduction in modulus in both cases (Figures 3.17 and 3.23), which suggests that the water induced plasticization promoted higher toughness in the resin.
The lab molded polyimide gave very similar results to the Hexcel molded samples for all tests; compare Figures 3.16 and 3.17 with Figures 3.22 and 3.23. In particular, the initial transverse strengths and moduli were close before immersion, with the Hexcel strength being a little lower and the modulus a little higher, as expected from the higher $V_t$ (Table 3.4). These polyimides were weaker than the epoxy (40-45MPa, as compared with 60MPa for the epoxy), possibly due to the slightly greater apparent "ductility" of the epoxy (0.29 as compared with 0.17 to 0.20 for the polyimide; Table 3.1). The NASA polyimide has about the same apparent ductility and about the same strength as the epoxy, suggesting a correlation between ductility and strength in the transverse test. The fractographs, Figures 3.44 and 3.45 show that when the Hexcel samples failed, they left less polymer adhering to the fibers. Moreover, the polymer appears to be less severely deformed in the Hexcel case, see Figure 3.45.

All the composites stand up well to 60°C treatment, but all showed very significant losses at 90°C. The 60°C strength loss for the lab-molded polyimide indicates imperfect molding, rather than a weakness in the material itself.

4.3 Curved Beam Strength

The force-distance plot for the curved beam strength test Figures 3.24, 3.26 and 3.28 follows the same form as in the ASTM D6415 standard. The values for the untreated samples, i.e. 0.63±0.06 kN for the carbon-epoxy and 0.57±0.11 kN for the carbon-polyimide indicate no significant difference between the resins, apart from the variability in the polyimide case. Converting to through the thickness strengths, $\sigma_{th}$ gives
respectively 50± MPa and 45±9 MPa. These values are calculated from equations given in ASTM D6415, i.e.

\[
\sigma_{in} = CBS f(\kappa) \rho^\nu g(\kappa) 
\]  

(26)

where:

\[
f(\kappa) = 1 - \frac{1 - \rho^{\nu+1}}{1 - \rho^{\nu}} \left( \frac{r_o}{r_i} \right)^{\nu+1} - \frac{1 - \rho^{\nu+1}}{1 - \rho^{\nu}} \rho^{\nu+1} \left( \frac{r_o}{r_m} \right)^{\nu+1} 
\]

(27)

\[
g(\kappa) = \frac{1 - \rho^2}{2} \left( \frac{\kappa + 1}{\kappa + 1 - \rho^2} \right) + \frac{\kappa \rho^2}{(\kappa - 1)(1 - \rho^2)} 
\]

(28)

\[
\kappa = \frac{E\nu}{E_i} 
\]

(29)

\[
\rho = \frac{r}{r_o} 
\]

(30)

\[
r_o = \left\{ \frac{(1 - \rho^{\nu+1})(\kappa + 1)(\rho^{\nu+1})^{\nu+1}}{(1 - \rho^{\nu+1})(\kappa - 1)\rho^{\nu+1}} \right\}^{1/(\nu+1)} 
\]

(31)

Where \(E_i\) and \(E_0\) are the modulus in the radial and tangential directions, respectively. \(r_i\) and \(r_o\) are the inner and outer radii of curved segment.

This carbon-epoxy result is about 20% lower than the transverse strength, \(\sigma_{20}\), of 62±4 MPa, while the polyimide is within experimental error of the transverse strength. These results are not surprising because the same factors determine both. These are interface strength and matrix strength [20].

The testing fixture was adapted from the standard to accommodate the very large deformations found when environmental treated samples were tested, as described in section 2.4.2. The near equivalence of \(\sigma_{20}\) and \(\sigma_{30}\) suggests that this modification did not
invalidate the tests for untreated samples. However, the results after water, oil and HCl immersion, which in some cases indicate an increase in strength, are almost certainly invalid, since the transverse strength did not show the same trends. A possible cause of this failure of the test is that the plasticization of the resin induced by the fluids caused $r_{0}$ to increase and the legs of specimen to bend during the test. A 41.4% increase in $r_{0}$ could double the apparent $\sigma_{10}$ (see Equation 26).

### 4.4 Fracture Toughness

The fracture toughness of the carbon-epoxy appears to be not affected by water up to 5.5 kh, but then declines about 20% over the next 1kh at 60°C and about 25% at 90°C, see Figure 3.33. The carbon-polyimide is somewhat tougher and suffers a less serious decline (about 20% α) with no significant difference between 60°C and 90°C. The force-distance curves, moreover, were changed only to about the same degree, see Figures 3.36, 3.38 and Table 3.3. The fracture behaviour was not entirely brittle, failure not being very sudden, as shown by these force-distance curves.

The effect of 20% HCl appeared to be rather serious in the case of the carbon-epoxy, with an overall loss of about 30% after 7kh, Fig. 3.35. Carbon-polyimide was less seriously affected, with no significant effect up to 5.5kh, and then a loss of about 20% (see Figure 3.39). The overall effect of paraffin oil at 80°C was about the same as 20% HCl, both as regards force-displacement plot, Figures 3.34, 3.38 and Table 3.3 and fracture toughness, Figures 3.35, 3.39 and Table 3.3.

All the above results support the earlier results for transverse strength and curved beam strength, in that the effect is probably due to a softening of the polymer. The fiber itself is considered to be unaffected by 20% HCl or by paraffin oil.
With glass, on the other hand, 20% HCl caused rapid initial loss of toughness, Figure 3.41, but with little further loss after about 1kh. It seems highly probable in this case that the acid weakens the fiber as well as the polymer. However, it is surprising that the displacement at failure is not reduced significantly.
5 Conclusions

Absorption

1. The carbon-polyimide has lower D and $M_\alpha$ values than the carbon-epoxy.

2. The voids in the polyimide composite samples contain the water, but are not filled up.

3. For the carbon-polyimide samples, the NASA polyimide is more resistant to water than the Hexcel polyimide. It absorbs less and the water diffuses more slowly. Moreover, the lab-made carbon polyimide laminate has a higher $M_\alpha$ and much higher $D_\alpha$ than the Hexcel made laminate.

4. The 20% HCl attacks the epoxy systems severely but has a much smaller effect on the polyimide systems. The HCl appears to be less reactive with the polyimide than the water alone.

5. Neither the carbon-epoxy nor the carbon-polyimide is much affected in kerosene.

Transverse Strength

1. The water induced plasticization promotes higher toughness in the resin and causes the large reduction in modulus in both Hexcel molded and lab molded carbon-polyimide at 90°C.

2. High temperature water has a stronger effect than low temperature water: all the composites stand up well to 60°C treatment, but all except the NASA samples showed very significant losses at 90°C.
3. The NASA samples have good water resistance performance in transverse strength tests: the strength and the apparent modulus of the NASA samples virtually remain unchanged in both 60°C and 90°C water environments.

**Curved Beam Strength**

1. The CBS results support the transverse strength results very well for the dry samples, but the method does not work very well for the wet samples due to plasticization of the resin.

**Fracture Toughness**

1. During the first 5 kh immersion, carbon-epoxy is more water resistant according to fracture toughness tests than the carbon-polyimide.

2. The effect of 20% HCl appeared to be rather serious in the case of the glass-epoxy probably because of attack on the glass-fibres. The carbon composites were less seriously affected.
References


45. L. W. Cai and Y. Weitsman, Non-Fickian Moisture Diffusion in Polymeric Composites, J Comp Mate. 28 (1994), 130-154